AD-A228 202

TECHNICAL REPORT NO. 11

Gas Solubility in Glassy Polymers - A Correlation with Excess Enthalpy

by

D.H. Rein, R.F. Baddour and R.E. Cohen
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

October 23, 1990

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	**3. DISTRIBUTION / AVAILABILITY OF REPORT**
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	Approve for public release and sale; distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
Technical Report No. 10	

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
MIT		Office of Naval Research, Chemistry

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Department of Chemical Engineering Cambridge, MA 02139	800 North Quincy Street Arlington, VA 22217-5000

8a. NAME OF FUNDING / SPONSORING ORGANIZATION ONR	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-87-K-0517

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
800 N. Quincy Street Arlington, VA 22217-5000	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)

Gas Solubility in Glassy Polymers - A Correlation with Excess Enthalpy

12. PERSONAL AUTHOR(S) D.H. Rein, R.F. Baddour, R.E..Cohen

13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) October 23, 1990	15. PAGE COUNT 26

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Gas transport, Glass transition, *Polymers*
			Free volume, Gas solubility , (JS)

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Solubility coefficients for CO_2, Ar and CH_4 in polystyrene (PS) films with glass transition temperatures (Tg) of 52 to 107 °C were measured in a pressure decay sorption apparatus at 1 atm over a temperature range of 20 to 90 °C. The gas solubility at 30 °C increased as the Tg of the PS increased; the heat of solution was largest for the PS with the highest Tg. This observed dependence of gas solubility on Tg was analyzed in terms of enthalpy - temperature relationships for glassy polymers. The solubilities for PS samples with different glass transition temperatures converged when comparisons were made based on states of equal enthalpy instead of the temperature of measurement.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL R.E. Cohen	**22b. TELEPHONE (Include Area Code)** 617-253-3777	**22c. OFFICE SYMBOL**

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted.
All other editions are obsolete.

Gas Solubility in Glassy Polymers - A Correlation with Excess Enthalpy

D. H. Rein, R. F. Baddour, R. E. Cohen

Department of Chemical Engineering
Massachusetts Institute of Technology
Canbridge, Massachusetts, 02139

Abstract

Solubility coefficients for CO_2, Ar and CH_4 in polystyrene (PS) films with glass transition temperatures (Tg) of 52 to 107 °C were measured in a pressure decay sorption apparatus at 1 atm over a temperature range of 20 to 90 °C. The gas solubility at 30 °C increased as the Tg of the PS increased; the heat of solution was largest for the PS with the highest Tg. This observed dependence of gas solubility on Tg was analyzed in terms of enthalpy - temperature relationships for glassy polymers. The solubilities for PS samples with different glass transition temperatures converged when comparisons were made based on states of equa enthalpy instead of the temperature of measurement.

Introduction

A unique value for the solubility of a gas in a glassy polymer is difficult to determine due to the complexity of specifying the state of a glass at a given temperature. Because the volume or enthalpy of a glass is strongly dependent on its thermal history, it is reasonable to expect multiple values for the gas solubility at a given measurement temperature. Although the various enthalpy or volume states are always relaxing towards a unique equilibrium state for the measurement temperature, any given nonequilibrium state may be essentially frozen in because the relaxation rates of a glass are slow relative to experimental time scales.

To quantify gas transport measurements in glassy polymers, recent workers [1 - 4] have been careful to specify the thermal history of the material. Sub - Tg annealing has been shown to have a measurable effect on the enthalpy and volume of the polymer and on the gas solubility [1 - 3]. Lower solubilities were measured in the glassy polymers which had been aged longer and were therefore closer to the equilibrium state of volume or enthalpy [1 - 4]. The dual mode sorption [5] model has been used to attribute the decreased solubility to the shrinkage of Langmuir sorption sites upon ageing. Here, we present an explanation for the dependence of the gas solubility on the state of the glass based on temperature-enthalpy relationships for glassy polymers.

Theoretical Framework

In this section we provide a theoretical framework in which we can anticipate the experimental observations to be presented below. We make use of the nonequilibrium nature of amorphous polymers below the glass transition temperature and the fact that at a specified cooling rate the amount of undercooling below Tg determines the initial amount of departure from equilibrium at any given observation temperature To. Therefore if a given polymeric material of fixed chemical composition can be manipulated (see below) at the molecular level to give a series of specimens with significantly different Tg values, it becomes possible to conduct a set of experiments at a single temperature To but at significantly different values of undercooling (Tg - To). For the case of gas

sorption experiments this is a particularly useful idea since the measurements are carried out with the gas always at the measurement temperature To but with the absorbing substrate (glassy polymer) at a variable effective temperature (to be defined below). We therefore have the possibility of separating the effect of temperature of the substrate from that of the gas in the temperature dependence of the sorption process, something not achievable when both the gas and the substrate are heated or cooled together.

Enthalpy - Temperature Relationships

Figure 1 is a schematic of the enthalpy - temperature profile for two glassy polymers of the same chemical composition, P1 and P2, but with different glass transition temperatures Tg1 and Tg2 (Tg1 < Tg2). Both materials follow the same liquid temperature - enthalpy equilibrium line above the glass transition temperatures where $\partial \underline{H}/\partial T = Cp_L$. As P2 becomes a glass upon cooling below Tg2, the temperature - enthalpy behavior departs from the equilibrium line and follows the nonequilibrium glassy line described by $\partial \underline{H}/\partial T = Cp_g$. P2 would follow the equilibrium line below Tg2 if the cooling rate was sufficiently slow, but these rates are not experimentally accessable; an amount of excess enthalpy is frozen into the glassy material.

P1 becomes a glass at Tg1, at which point it also deviates from the equilibrium liquid curve and follows the glassy curve given by $\partial \underline{H}/\partial T = Cp_g$. At a given temperature To below Tg1, P1 and P2 are in two different enthalpy states. The excess enthalpy in P1 is equal to $(Cp_L-Cp_g)(Tg1-To)$, and the excess enthalpy in P2 is equal to $(Cp_L-$

Cp_g)($Tg2-To$). At To, the difference between the enthalpy of P1 and P2 is equal to ($Tg1-Tg2$)(Cp_L-Cp_g) (a negative quantity). A sorption experiment conducted at a temperature To below $Tg1$ would therefore compare the solubility of a gas at a given temperature in a material of common chemical structure (i.e. polystyrene) but in different enthalpy states. It is the purpose of this paper to correlate this difference in enthalpy states with measured differences in the solubilities in the two glassy polymers.

Since both enthalpy and volume are known to be influenced similarly by sub-Tg annealing of glassy polymers, there is reason to believe that a correlation of excess volume, instead of enthalpy, with gas solubility could be equally well constructed. We prefer to use the frozen-in enthalpy because by definition ($H = U + PV$) it accounts for the volumetric state of the material and its internal energy. The latter reflects the molecular motions of the material into which gas is sorbing. While large scale thermal motion of chain molecules is frozen for glassy polymers, it is reasonable to expect that some short range motions persist and that these motions are diminished as T drops farther below Tg. To the extent that these short range thermal agitations reduce the equilibrium amount of gas which can be sorbed into a glassy substrate at sorption equilibrium, a correlation based on H, rather than V, should be superior. If thermal motions in all the substrates are identical or if they have no influence on the gas solubility at sorption equilibrium, then volume or enthalpy correlations can be used equally well to explain the gas sorption behavior in glassy polymers.

Development of T*

An adjusted temperature scale will be useful to compare the solubilities of samples with different Tg's so that the comparisons are made at equal polymer enthalpy states. We define a temperature T* as the temperature which a glass must assume in order to reach the enthalpy equal to that at the equilibrium state at To, the temperature of measurement Above Tg, T* is equal to the measurement temperature since the liquid or rubber is in an equilibrium state. Below Tg, T* is equal to the temperature necessary to reduce the enthalpy by an amount equal to the excess enthalpy defined above. T* is defined as :

$$T^* = To - [(Tg - To)(Cp_L - Cp_g)]/Cp_g \qquad (1)$$

Thus for a given value of To, the value of T* depends on the Tg and the difference in heat capacities between the glassy and rubbery states. Figure 1 shows schematically the calculation of T* at a given temperature To for P1 and P2. P2 has a higher Tg than P1 and therefore contains more excess enthalpy at To. A greater reduction in temperature (lower T*) is necessary for P2 to attain the equilibrium enthalpy associated with temperature To. Thus P2 is considered to exist at a lower effective temperature; it is "colder" than P1 in the solubility measurements at To.

Gas solubility and T*

The gas solubility is expected to be higher in P2 than in P1 at temperatures below Tg2 since P2 has a lower effective temperature T* [It is commonly observed that S increases as measurement temperature decreases; generally this trend has been attributed [6] to the increased condensibility of the gas rather than the state of the

material into which the gas is sorbing.] At a fixed temperature, measuring the gas solubility in a series of glasses with increasing Tg's is equivalent to lowering the temperature of the polymer thereby explaining the observed result of increasing solubility with increasing Tg.

The temperature scale T* can also be used to analyze the temperature dependence of the gas solubility in a glass compared to the behavior in the corresponding rubber. The temperature dependence of the gas solubility in a polymer sample above its Tg would follow the temperature of the measurement since T* = To above Tg. In the glassy state, the temperature of the measurement changes directly with To while the state of enthalpy of the polymer changes with T*. Since

$$T* = To(1 \div ((C_{p_L}-C_{p_g})/C_{p_g})) - Tg(C_{p_L}-C_{p_g})/C_{p_g}, \quad (2)$$

$$\partial T* = \partial To(1 \div ((C_{p_L}-C_{p_g})/C_{p_g})) \quad (3)$$

Thus T* changes more rapidly than To. Plotted against To, the temperature dependence of S in the glassy state should be stronger (more exothermic) than in the rubbery state.

These thermodynamic arguments regarding solubility and its temperature dependence were used to analyze the measured solubility behavior of CO_2, CH_4, and Ar in a model set of polystyrene samples with different Tg's.

EXPERIMENTAL

The CO_2 gas (Colony, Inc.) and Ar gas (Colony, Inc.) had purities in excess of 99.99%, and the CH_4 gas (Matheson, Inc.) had a purity

listed at 99.0%. Two polystyrene (PS) homopolymers were obtained from Polysciences, Inc. with nominal molecular weights of 250,000 (PS4) and 20,000 (PS1). Two additional PS samples were prepared by fractionating PS1. Methanol was slowly dripped into a 10% PS1 / toluene solution until a significant amount of polymer had precipitated. This filtered precipitate (PS2) was fractionated again to yield PS3. All four polystyrene samples were annealed in vacuum just below Tg for 4 days to remove residual solvent.

Gel permeation chromatography (GPC), differential scanning calorimetry (DSC, 10 °C/min.), and proton NMR were used to characterize the polymer samples. The gas solubility (S) and diffusion (D) coefficients were measured at 1 atmosphere pressure in a pressure decay sorption apparatus described in detail elsewhere [7]. The D and S values for CO_2 , Ar and CH_4 in PS1, PS2, PS3 and PS4 were determined over the temperature range 20 to 90 °C.

RESULTS AND DISCUSION

Polystyrene Fractionation

Table 1 summarizes the DSC and GPC results for the four PS samples. The glass transition temperature (Tg) for polystyrene varied from 52 °C to 107 °C as Mn varied from 2,100 to 200,000 g/mole. None of the measured Tg values was influenced by the presence of any sorbed gases at the pressures and temperatures used in this study. The NMR spectra of the four samples were all identical and indistinguishable from polystyrene spectra in the literature, precluding the existance of externally added plasticizers or

other significant impurities. The GPC chromatograms for PS1, PS2 and PS3 are shown in Figure 2. Low molecular weight oligomers of styrene appear in large concentration in PS1 (Figure 2). Evidently the presence of these oligimers is responsible for the depression of the Tg of PS1 to 52 °C. The fractionation steps used to prepare PS2 and PS3 successively removed the low molecular weight oligomers and increased the proportion of the longer chains. Removal of the oligomers increases Tg of PS2 to 72 °C and the Tg of PS3 to 90 °C. The GPC results for PS4 indicated a broad distribution of long chains with no low molecular weight species.

Solubility Coefficient

The behavior of the solubility coefficients (measured at 1 atm) for CO_2, Ar and CH_4 as a function of temperature for PS1 and PS4 is shown in figures 3a - c. The heats of solution (Es, Kj/mole) obtained from these plots for PS1 (Tg = 52 °C) were -12.4, -4.6, and -6.2 for CO_2, CH_4, and Ar, respectively; the heats of solution (Kj/mole) for PS4 (Tg = 107 °C) were larger in magnitude at -22.0, -15.7 and -11.3, respectively. The observed order of increasing gas solubilities (Ar < CH_4 < CO_2) reflects the trend of increasing gas boiling temperatures and increasing Lennard - Jones gas potentials. This is consistant with reported correlations of increasing gas solubility with increasing ease of gas condensibility [5].

For all three gases examined, the heats of solution for the polystyrene with the higher Tg (PS4) were more exothermic than the heats of solution for the polystyrene with the lower Tg (PS1). This behavior can be understood by considering the enthalpy of PS1 and PS4 at the measurement temperatures. Over the temperature

range 20 - 90 °C, PS1 was primarily in the melt (liquid state) and the glass transition zone, while PS4 was in the glassy state. The enthalpy of PS1 was therefore either equal to or close to the equilibrium state enthalpy, while PS4 always contained an amount of excess enthalpy. Comparing the gas solubilities on a temperature scale based on the measurement temperature To instead of T* predicts a stronger temperature dependence (more exothermic) for the solubility in a glass than in the corresponding rubber, which is what was observed.

The CO_2 solubility in PS at 30 °C decreased as the Tg of the PS sample decreased (see Figure 4). This dependence of the solubility on Tg was less pronounced at higher test temperatures, and disappeared when all the materials became rubbery (see Figures 3a-c). Again, the solubility behavior is consistent with the different enthalpy states that the PS samples assume at 30 °C. At 30 °C PS4 has the largest excess enthalpy since it has the highest Tg, and PS1 has the smallest amount of excess enthalpy. Using the adjusted temperature scale T* to compare the polymer gas solubilities on an equal enthalpy basis, PS4 reaches a lower temperature T* than PS1 in order to attain the enthalpy equal to the equilibrium enthalpy at 30 °C. Since CO_2 solubility increases as the temperature decreases, the polymer at the lower temperature T* (PS4) should have a higher solubility, as observed. Assuming the differences in solubilities among polymer samples depends on the amount of excess enthalpy, all observed differences in gas solubilities should disappear as the highest Tg of the samples is approached. This is observed in figures 3a - c.

The effect of excess enthalpy on the gas solubility and the heat of solution can be quantified using equation 3 with an estimate of the value of $(Cp_L-Cp_g)/Cp_g$. For polystyrene, a value of 0.6 was chosen based on [8]. According to our proposal outlined above, solubilities of gases in polystyrene with equal states of enthalpy should be identical. This comparison is possible by plotting the gas solubilities in PS as a function of T^*. Figures 5a - c display the CO_2, Ar and CH_4 solubility coefficients for PS1 and PS4 as a function of $1/T^*$. The heats of solution (Kj/mole) for CO_2, CH_4 and Ar in PS calculated from figures 7 through 9 lie in the range -12.1 to -9.1, -7.0 to -3.5 and -6.3 to -4.7, respectively. The range of Es is larger for CH_4 and Ar due to the increased uncertainty in the measurement.

Table 2 summarizes the heats of solution for CO_2, CH_4 and Ar in PS1 and PS4 calculated from solubilities plotted against the measurement temperature (Es) and against the adjusted temperature scale T^* (E^*). The E^* values in table 2 are the midpoint of the range of values calculated from each of figures 5a - c. The values for E^* are close to those of Es for PS1 since PS1 is in the rubbery state and the early glass transition region over the temperature range explored. The use of equal enthalpy states to compare solubilities in glasses instead of the measurement temperature results in convergence of the solubility and heat of solution values for PS samples with different glass transition temperatures. This convergence is most clearly seen for the CO_2 data.

Summary

Solubility of gases in polymers depends on the chemical nature of the gas and polymer and on the state of enthalpy of the polymer. Above Tg the polymer is always in a state of equilibrium enthalpy so S depends only on the test temperature To, and S generally increases as To decreases. However in the glassy state, excess enthalpy exists at a given test temperature and the amount of this excess enthalpy depends primarily on the value of the Tg for the material [Tg can vary widely for a given polymer depending upon molecular weight and its distribution]. Therefore, glassy polymers must be considered to exist at an effective temperature, T*, which is less than To, the measurement temperature; the value of T* is lower for samples with higher Tg's. This qualitative analysis explains the trends observed in a set of data for the solubility of gases in a series of polystyrenes of varying Tg's. The most notable trend is the large increase (by as much as a factor of 1.9) in S (measured at 30 °C) with increasing substrate Tg.

Acknowledgements

References

1. Tsitsilianis, C. *Polym. Commun.*, 1989, 30, 331.

2. Chan, A. H.; Paul, D. R. *Polym. Eng. Sci.*, 1980, 20 (1), 87.

3. Chan, A. H.; Paul, D. R. *J. Appl. Polym. Sci.*, 1979, 24, 1539.

4. Koros, W. J.; Paul, D. R. *J. Polym. Sci.*, 1978, 16, 1947.

5. Stannett, V. T.; Koros, W. J.; Paul, D. R.; Lonsdale, H. K.; Baker, R. W., " Recent Advances in Membrane Science and Technology " in *Advances in Polymer Science*, 32, Springer - Verlag New York, 69, 1979.

6. *Recent Developments in Separation Science*, Vol. II; Li, N. N., Ed.; CRC Press: Cleveland, 1976.

7. Rein, D. R.; Csernica, J.; Baddour, R. F.; Cohen, R. E. *Macromolecules* , 1990, *23*, 4456.

8. Polymer Handbook; Brandrup, J.; Immergut, E. H., Eds.; John Wiley & Sons: New York, 1975.

Table I

Characterization of PS samples

Polymer	Tg [C]	Mw	Mn
PS1	52	25,600	2,100
PS2	72	26,000	3,000
PS3	91	34,000	5,700
PS4	107	250,000	200,000

Table 2
Heats of solution in PS1 and PS4

Gas	Es (PS4)	Es (PS1)	Es*
CO_2	-22.0	-12.1	-10.5
CH_4	-15.7	-4.6	-5.2
Ar	-11.3	-6.2	-5.5

Note : Es* is the heat of solution for all of the
PS samples based on the T* temperature scale

Figure Legends

Figure 1.   Temperature - enthalpy curve for polymers PS1 and PS2 with glass transition temperatures at Tg1 and Tg2, respectively. T* is defined as the temperature which the polymer would have to assume to obtain the equilibrium value of enthalpy at temperature To

Figure 2.   GPC chromatogram of PS1, PS2 (PS1 fractionated once), PS3 (PS1 fractionated twice).

Figure 3a.   Temperature dependence of the equilibrium CO_2 solubility coefficients for PS1 and PS4.

Figure 3b.   Temperature dependence of the equilibrium Ar solubility coefficients for PS1 and PS4.

Figure 3c.   Temperature dependence of the equilibrium CH_4 solubility coefficients for PS1 and PS4.

Figure 4.   Effect of polystyrene Tg on the CO2 solubility at 30°C.

Figure 5a.   Measured CO_2 solubility in PS1 and PS4 compared at equal enthalpy states using the temperature scale T* and $(Cp_L - Cp_g)/Cp_g = 0.6$

Figure 5b.   Measured Ar solubility in PS1 and PS4 compared at equal enthalpy states using the temperature scale

T^* and $(Cp_L - Cp_g)/Cp_g = 0.6$

Figure 5c.   Measured CH_4 solubility in PS1 and PS4 compared at

equal enthalpy states using the temperature scale
T^* and $(Cp_L - Cp_g)/Cp_g = 0.6$